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Thermodynamic properties and alloying behaviour of liquid binary alloy : CdZn

S M Rafique* and Ashwani Kumar

University Department of Physics, T M Bhagalpur University, Bhagalpur-812 007, Bihar, India

E-mail sm_rafq@yahoo com

Abstract : The complex formation model first proposed by Bhatia and Hargrove [1] assumes the existence of chemical complexes or pseudomolecules in liquid binary alloys On the basis of this concept Singh and his coworkers [2–5] have studied various thermodynamical properties of different binary alloys We have also studied different alloys within this framework [6–8] The present paper envisages the study of some thermodynamic properties *viz*, Gibbs free energy of mixing (G_M), enthalpy of mixing (H_M) and entropy of mixing (S_M) of CdZn binary alloy The results are in reasonable agreement with experiment and throw light on the ionic interactions of the constituent atoms leading to the alloying behavior of the alloys under investigation

Keywords : Complex formation model, entropy of mixing, CdZn alloy, liquid alloys, thermodynamic model

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1. Introduction

The concept of formation of complexes or pseudomolecules in liquid binary alloys proposed by Bhatia and Hargrove [1] is being widely used for the study of thermodynamic properties and alloying behaviour of binary alloys [2–5]. In our earlier papers [6–8], we have studied thermodynamic, structural and surface properties of some binary alloys within this framework.

In this paper, we present the computation and results of free energy of mixing (G_M), heat of mixing (H_M) and entropy of mixing (S_M) of liquid CdZn alloy. Comparison has also been made with the available experimental data. The results of the computed properties and parameters throw light on the nature and behavior of this alloy.

2. Formalism and computation

The formalism of the present work has been presented in our earlier papers [6–8]. Here we confine with the final expressions of the computed properties. In the binary alloy, we assume that chemical complexes or pseudomolecules are present. They are represented as $\mu A + \nu B = A_\mu B_\nu$. Here μ and ν are integers.

Let the binary alloy contains nA atoms of A, nB atoms of B where $nA = c_A N$

*Corresponding Author

and $nB = c_B N$ where N is the Avogadro's number and c_A and c_B are the concentrations of the two species. Then it is assumed to consist of $n_1 N$ free atoms of A, $n_2 N$ free atoms of B and $n_3 N$ complexes $A_\mu B_\nu$ acting as independent scattering centers in the alloy. From the conservation of atoms :

$$n_1 = 1 - c_B - \mu n_3 ,$$

$$n_2 = c_B - \nu n_3 ,$$

$$n = n_1 + n_2 + n_3 . \tag{1}$$

The number of complexes n_3 is obtained through the condition

$$(\partial G_M / \partial n_3)_{T,P,c} = 0 , \tag{2}$$

where G_M is the Gibb's free energy of mixing and T, P, c are the temperature, pressure and concentration respectively. The conformal solution approximation enables us to express G_M as

$$G_M = -n_3 g + RT \sum_{i=1}^{n} n_i (\ln n_i - \ln n) + \sum_{i<j} \sum \left(\frac{n_i n_j}{n} \right) W_{ij} , \tag{3}$$

where W_{ij} are the interaction energies which are independent of concentration, g is the formation energy, R is the gas constant. From eqs. (2) and (3), we get

$$\left(\frac{n_1^\mu n_2^\nu}{n_3 n^{\mu+\nu-}} \right. = e^{-g/RT} \exp(y_1 + y_2 + y_3) , \tag{4}$$

where

$$y_1 = \frac{W_{12}}{RT} \left[(\mu + \nu - 1) \left(\frac{n_1 n_2}{n^2} \right) - \left(\frac{\mu n_2}{n} \right) - \left(\frac{\nu n_1}{n} \right) \right] ,$$

$$y_2 = \frac{W_{13}}{RT} \left[(\mu + \nu - 1) \left(\frac{n_1 n_3}{n^2} \right) - \left(\frac{\mu n_3}{n} \right) - \left(\frac{n_1}{n} \right) \right] ,$$

$$y_3 = \frac{W_{23}}{RT} \left[(\mu + \nu - 1) \left(\frac{n_2 n_3}{n^2} \right) - \left(\frac{\nu n_3}{n} \right) + \left(\frac{n_2}{n} \right) \right] . \tag{5}$$

The equilibrium value of n_3 is obtained by solving numerically eq. (4) and then it is used to obtain G_M through eq. (3). The interaction energies W_{ij} and formation energy (g) are determined through the Bhatia-Hargrove technique [1].

The heat of mixing H_M and entropy of mixing S_M are given by

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_{P,c,N} , \tag{6}$$

$$S_M = \left(\frac{H_M - G_M}{T} \right) \tag{7}$$

The computation of the above mentioned parameters has been done through eqs. (1–7) and the computed results are presented in Figures 1 and 2 paragraph alongwith the experimental data for comparison against Zn concentration c_{Zn}.

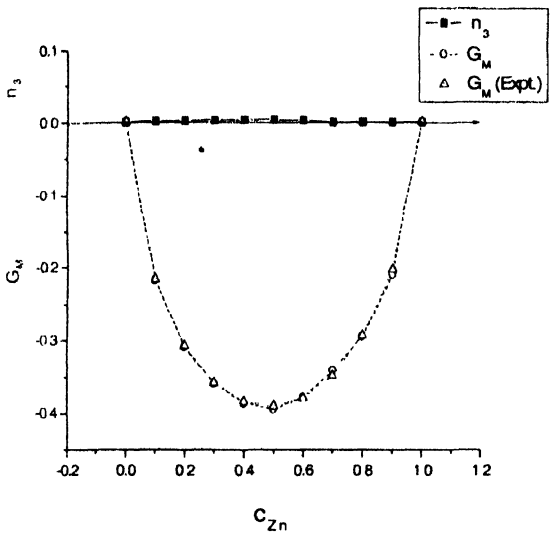

Figure 1. Number of complexes and energy of mixing of CdZn liquid alloy (800 K), against Zn concentration c_{Zn}.

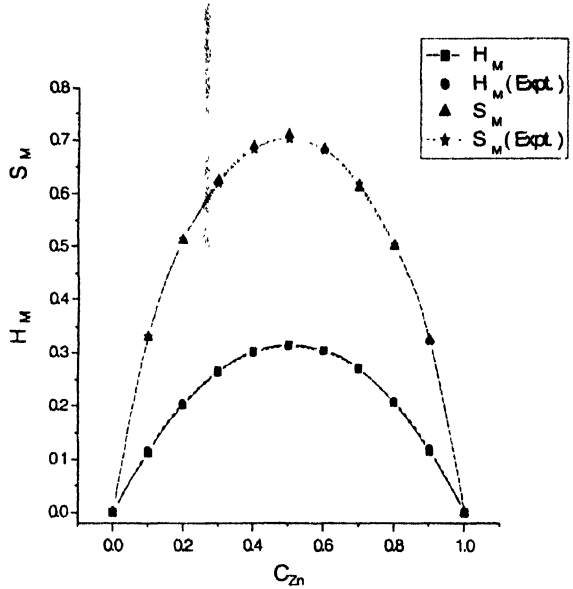

Figure 2. Heat and entropy of mixing of CdZn liquid alloy (800 K), against Zn concentration c_{Zn}.

3. Observation and inferences

The computation of the energy of mixing (G_M), heat of mixing (H_M) and entropy of mixing (S_M) was carried out for CdZn alloy at different concentrations at 800 K. It was observed that the numbers of complexes are very small. This indicates that CdZn form simple binary alloy. This seems reasonable because both of the constituents have the same valency and lie in the same group IIB of the periodic table. The physical and chemical properties are also similar in various aspects. Inspection of Figure 1 reveals that the number of complexes n_3 is quite small and the computed value of G_M (in terms of RT) agrees well with the experimental results of Hultgren *et al.* [9]. Hence, simple binary alloy CdZn has been considered onwards with $\mu = \nu = 1$ and the equilibrium values of n_3 have been arrived at. However, if we apply the equilibrium condition (4) no reasonable agreement is obtained with experimental data of G_M [9] which excludes the possibility of complex formation.

The computed values of H_M and S_M are also in good agreement with experimental result (*vide* Figure 2). The interaction energies are computed on the basis of Bhatia and Hargrove technique. The equilibrium values of chemical complexes n_3 have been obtained through numerically solving eq. [2]. The interaction energies W_{ij} are adjusted until a good fit for G_M is obtained. Once the energy parameter is selected, they remain the same for all concentrations. The computed values are $g = 1.359$, $W_{12} = 1.29$, $W_{13} = -1.0$, $W_{23} = 1.8$ (in terms of RT). The derivatives needed for the computation

of H_M and S_M are found to be $\partial g/\partial t$ = 0.99485, $\partial W_{12}/\partial t$ = 0, $\partial W_{13}/\partial t$ = 0.3, $\partial W_{23}/\partial t$ = 1.32. As the complex formation energy g/RT is 1.359 which is appreciably smaller than 3.55, the CdZn alloy may be assumed to be a weakly interacting system like CuSn, AgAl, MgSn *etc.* For strongly interacting systems, g/RT has much larger value *e.g.*, MgBi (16.7), TlTe (10.84), HgK (9.965), HgNa (8.294). Also we find that W_{12} and W_{23} are positive *i.e.*, repulsive in nature while W_{13} is attractive which also justifies the weakly interacting nature.

An inspection of Figure 1 reveals that the Gibbs free energy of mixing (G_M) of CdZn binary alloy is in reasonably good agreement with experimental observations and is symmetric about c = 0.5 (Hultgren *et al* [9]). From Figure 2 we observe that the heat of mixing H_M and entropy of mixing S_M are also in good agreement with experiment [9] and they also show symmetric behaviour. However, it is to be noted that H_M of CdZn alloy is positive for all concentrations like CdTl, AlGa, AlPb, AlZn, CdGa, CdIn, GaZn, InTl, InZn, KNa *etc.* alloys [9]. In general, the heat of mixing is found to be negative for many alloys. This gives a special character to this alloy. CdZn forms a simple eutectic phase diagram like GaZn, NaRb, AlBe, CdPb *etc.* It is to be mentioned that solutions whose components exhibit negative deviations from Roult's law, form exothermically *i.e.*, $H_M < 0$. In contrast the solution whose components exhibit positive deviations from Roult's law will form endothermically *i.e.*, $H_M > 0$. This is the case for CdZn alloy.

4. Summary and conclusion

In the present work, the CdZn alloy has been studied within the framework of complex formation technique proposed by Bhatia and Hargrove [1] in respect of its thermodynamical properties *viz.*, G_M, H_M and S_M. The following important conclusions may be drawn from the present investigation :

(i) As CdZn presents an eutectic phase diagram and both the constituents belong to the same group II B of the periodic table, the probability of complex formation is meagre which is indicated by the very small value of n_3 at all concentrations. The previous experimental and theoretical workers have also not suggested any other complex in the liquid or solid phase.

(ii) All the computed properties are in fairly good agreement with experiment if simple CdZn alloy is considered taking $\mu = \nu = 1$. Other values of μ and ν do not provide experimental agreement excluding the possibility of formation of complexes.

(iii) All the computed properties show symmetrical behavior about equiatomic concentration.

(iv) The heat of mixing of CdZn is positive for all concentrations which places it in the category of CdTl, CdGa, CdIn *etc.* in contrast to CdPb, GaZn, AlBe *etc.* This throws light on the alloying behavior of this alloy.

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